

NICKEL CONTAINING HIGH COPPER A

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5 Not Applicable

CROSS-REFERENCE TO RELATED APPLICATION

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR  
DEVELOPMENT

Not Applicable

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BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a high copper alloy that has improved stability at temperatures of at least 150°C. More particularly, resistance to stress relaxation at 15 elevated temperatures is improved in copper alloys containing controlled amounts of iron, tin, nickel and phosphorous when compared to copper alloys containing iron, tin, cobalt and phosphorous.

2. Description of Related Art

20 Throughout this patent application, all percentages are given in weight percent and all mechanical properties are determined at room temperature (20°C) unless otherwise specified.

The Copper Development Association (CDA, New York, NY) designates a wrought copper alloy with a copper content of less than 99.3% but more than 96% that does not fall into any other copper alloy group as a "high copper alloy". A subset of the high copper alloy group is copper alloys containing iron, tin and phosphorous. The high copper alloys in this subset are characterized by high electrical conductivity, but relatively poor resistance to stress relaxation at temperatures exceeding 125°C. They are commercially used in electrical and electronic applications, such as connectors and leadframes.

One high copper alloy is designated by the CDA as copper alloy C19500. This copper alloy has a specified composition of 1.0% - 2.0% iron, 0.3% - 1.3% cobalt, 0.10% - 1.0% tin, 0.01% - 0.35% phosphorous and the balance is copper. As reported in Volume 2 of the ASM Handbook, dependent on temper, the yield strength ranges from 45-70 ksi for the H01 temper to 85-92 ksi for the H08 (spring) temper. The electrical conductivity is reported to be 45% IACS, minimum. IACS refers to the International Annealed Copper Standard that assigns "pure" copper a conductivity value of 100% IACS at 20°C.

C19500 is typically formed into electrical connectors. High contact force is possible with this alloy due to its moderate strength. Further, the moderately high electrical conductivity of the alloy enables the formed electrical connector to conduct large electrical currents without unacceptable resistance heating. C19500's usefulness for electrical connectors is generally limited to applications where the expected service temperature will not exceed around 100°C. The alloy has an unacceptably high rate of stress relaxation at temperatures exceeding 100°C. Stress relaxation is manifest as a gradual loss in contact force during prolonged thermal exposure. Reduced contact force can be accompanied by increasing contact resistance and may eventually result in an open circuit failure. The rate of stress relaxation increases as a function of increasing temperature. At temperatures above 100°C the service life of a C19500 connector is limited.

US Patent No. 3,698,965 to Ence discloses a copper alloy that contains 0.2% - 4.0% iron, 0.2% - 2.5% cobalt, 0.01% - 0.5% phosphorous, 0.1% - 1.0% tin and the balance is essentially copper.

US Patent No. 4,605,532 to Knorr et al. discloses a copper alloy that contains 5 0.3% - 1.6% iron, up to 0.5% tin, 0.1% - 0.4% phosphorous, 0.01% - 0.2% magnesium and balance copper. The 4,605,532 patent discloses that up to 50% of the iron may be replaced with nickel. One comparative alloy is disclosed as containing 1.05% iron, 0.12% magnesium, 0.37% phosphorous, 1.00% tin and the balance copper.

US Patent No. 6,132,528 to Brauer discloses a copper alloy that contains 0.8% - 10 4% iron, 0.3% - 1.8% nickel, 1% - 4% tin, up to 0.4% phosphorous, from an amount effective to enhance iron initiated grain refinement to 35% zinc and the balance copper. It is further disclosed that in a tin brass alloy, an addition of nickel improves the resistance of the tin brass alloy to stress relaxation.

United States Patent Numbers 3,698,965, 4,605,532 and 6,132,528 are 15 incorporated by reference herein in their entireties.

Japanese published patent publication JP11-264037 by Tetsuo discloses a copper alloy foil containing 0.05% - 3.5% iron, 0.01% - 0.4% phosphorous and the balance copper. Optionally, the alloy may contain one or both of 0.05% - 5% zinc and 0.05% - 20 3% tin. As a further option, the alloy may contain one or more of magnesium, cobalt, lead, zirconium, chromium, manganese, aluminum, nickel, silicon, indium and boron in an amount of 0.01% - 2% in total.

There exists a need for a copper alloy having a resistance to stress relaxation at elevated temperatures that is superior to copper alloy C19500 and that provides a combination of high strength, high electrical conductivity and good formability.

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#### SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a high copper alloy that has improved resistance to stress relaxation at elevated temperatures of up to at least 150°C. It is a feature of this invention that the high copper alloy contains controlled

amounts of iron, nickel, tin and phosphorous. It is another feature of the invention that the alloy has an electrical conductivity in excess of 40% IACS and an ultimate tensile strength in excess of 70 ksi. It is an advantage of the invention that the alloy is characterized by high electrical conductivity, high strength and good formability making 5 the alloy particularly, but not exclusively, useful for electrical connector applications.

In accordance with the invention, there is provided a copper alloy that consists, by weight, essentially of from 0.8% to 3% iron, from 0.3% to 2% nickel, from 0.6% to 1.4% tin, from 0.01% to 0.35% phosphorous and the balance is copper and inevitable impurities.

10 The above stated objects, features and advantages will become more apparent from the specification and drawings that follow.

#### IN THE DRAWINGS

15 Figure 1 shows in block diagram a sequence for processing the alloys of the invention.

Figure 2 graphically illustrates the effect of the amount of cold working from an intermediate thickness to final gauge on the yield strength of an alloy of the invention.

#### DETAILED DESCRIPTION

20 The copper base alloys of the invention contain controlled amounts of tin, iron, phosphorous and nickel.

Iron enhances grain refinement improving bend formability. The iron further combines with phosphorous to form dispersed iron phosphides that, in combination with dispersed nickel phosphides, increase alloy strength. Excess iron precipitates as 25 peritectic iron particles during casting. These peritectic particles form large stringers,

acicular iron particles having a length in excess of about 200 microns, during subsequent processing. The large stringers impact both the appearance of the alloy surface as well as the surface's electrical and chemical properties. The large stringers can change the solderability and electro-platability of the alloy. To avoid the formation of large 5 stringers, the alloy has a maximum iron content of 3%. If the iron content is too low, the beneficial improvements in bend formability and in increased strength are not achieved. A minimum iron content for the alloy is 0.8%.

Preferably, the iron content is between 1% and 2%. Most preferably, the iron content is between 1% and 1.5%.

10 Nickel improves the resistance of the alloy to stress relaxation at elevated temperatures, such as 125°C and 150°C, particularly when compared to a cobalt containing copper alloy having similar electrical and mechanical properties. If the nickel content exceeds 2%, a detrimental decrease in electrical conductivity occurs. When the nickel content is less than 0.3%, the improved resistance to stress relaxation is lost.

15 Preferably, the nickel content is between 0.5% and 1.3%. Most preferably, the nickel content is between 0.5% and 1%.

20 Tin enhances solution strengthening and response to work hardening. However, tin can make the alloy more difficult to process, particularly during hot processing, and also detrimentally affects electrical conductivity. When the tin content exceeds 1.4%, the cost of processing the alloy may be prohibitive for certain commercial applications and the electrical conductivity decreases to levels less suitable for an electrical connector. When the tin content is less than 0.6% by weight, the increase in strengthening response is lost.

25 More preferably, the tin content is between 0.7% and 1.1%. Most preferably, the tin content is between 0.8% and 1.0%.

Phosphorous deoxidizes the melt and inhibits the formation of copper oxide or tin oxide. The phosphorous combines with iron and nickel to form iron phosphides and nickel phosphides that are dispersed through the alloy matrix and increase the strength of

the alloy. Excessive phosphorous can interfere with the processing of the alloy, particularly with hot rolling and does not enhance desirable alloy properties. The phosphorous content of the alloy of the invention is from 0.005% to 0.35%.

5 A preferred phosphorous content is from 0.01% to 0.2%. A most preferred phosphorous content is between 0.01% and 0.1%.

The alloys of the invention may include inevitable impurities in amounts recognized to those skilled in the art as an impurity as well as small amounts of other, unspecified, alloying additions that do not significantly reduce alloy strength, resistance to stress relaxation and electrical conductivity.

10 These unspecified additions include manganese, zinc, magnesium, beryllium, silicon, zirconium, titanium, chromium and mixtures thereof. The unspecified additions are preferably present in an amount less than about 0.2% each, and most preferably, in an amount of less than about 0.01%. Most preferably, the sum of all less preferred alloying additions is less than about 0.1%.

15 Figure 1 illustrates a processing sequence for the alloys of the invention. The alloys are cast 10 by any known process such as direct chill casting or strip casting. For direct chill casting, the required amounts of iron, nickel, tin and phosphorous are added to molten copper with stirring to insure homogeneity. The molten metal is transferred to a suitable mold and cooled to form an ingot. The ingot is reheated to a temperature in  
20 excess of 700°C for hot working 12. Preferably, hot working 12 is by hot rolling that begins at a temperature of between 750°C and 950°C. Most preferably, hot rolling is commenced at a temperature of between 825°C and 875°C and remains above a temperature of about 700°C through out the hot rolling step that may involve either a single or multiple passes through a rolling mill.

25 Hot rolling forms the ingot into a relatively thick slab of copper alloy. The slab may be cooled either by a water quench or by air cooling. The surfaces of the slab are then optionally, but preferably, milled to removed surface oxides. Following milling, the copper alloy slab is cold worked 14, such as by rolling to an exemplary thickness of

0.090 inches. This cold rolling reduction may be in a single rolling step through the rolling mill or require multiple rolling steps. If multiple rolling steps are utilized, intermediate anneals at a temperature of between 400°C and 700°C for a time effective to recrystallize the slab may be utilized.

5        When the desired thickness is achieved, the copper alloy, now in strip form, is annealed 16 at a temperature of between 400°C and 700°C for from 2 to 6 hours. Preferably, the anneal 16 is for a nominal time of 4 hours at a nominal temperature of 575°C. The purpose of anneal 16 is to recrystallize the microstructure and to enhance dispersion of iron, iron phosphide and nickel phosphide particles.

10      Following the anneal 16, the copper alloy strip is further processed for moderate strength and good resistance to elevated temperature stress relaxation. The copper alloy strip is cold worked 18, such as by one or more cold rolling steps, to an intermediate thickness 20 that, as described below, is dependent on the desired final gauge.

15      The copper alloy strip is then annealed 22 at a temperature of between 400°C and 700°C for a time of from about one-half to six hours. The purpose of the anneal 22 is to recrystallize the microstructure, achieve a more equiaxed grain shape and to set the final gauge to make temper. More preferably, anneal 20 is at a temperature of from 475°C and 525°C for from two to four hours.

20      The copper alloy strip is then cold worked 24, such as by rolling to a desired final gauge in a one or more cold rolling steps.  $\Delta$ , the percent change in thickness between intermediate thickness 20 and final gauge 26, is selected to achieve a desired temper. Figure 2 graphically illustrates the effect of  $\Delta$  on the yield strength (Y.S.) of a copper alloy strip of the invention (nominal composition of 2% Fe, 0.5% Ni, 0.5% Sn, 0.03% P and the balance copper) both after cold work step 24 (reference line 28 in Figure 2) and 25 after relief anneal 30 (reference line 32 in Figure 2).

Once at final gauge 26, the copper alloy strip is relief annealed 30 at a temperature of from 200°C to 350°C for from 30 minutes to six hours. Preferably, the relief anneal 24 is at a temperature of from 250°C to 325° for from one to three hours.

While the copper alloys of the invention are particularly suited for being formed into an electrical connector, the alloys are equally useful for being formed into a leadframe, a wire or a rod.

The advantages of the copper alloys of the invention will be more apparent from 5 the Example that follows.

#### EXAMPLE

Copper alloys of the invention having the weight percent compositions reported in Table 1 and designated as H898 and H899 were evaluated. Control alloys were either 10 commercially obtained, in the case of C19500, or internally cast, in the case of C19205, C505 and C510, to CDA specifications.

Table 1

Alloy	Iron	Cobalt	Nickel	Phosphorous	Tin	Copper
H898	1.72	-----	0.49	0.015	0.40	balance
H899	1.80	-----	0.46	0.10	0.40	balance
C19500	1.5	0.8	-----	0.35	0.6	balance
C19025	-----	-----	1.0	0.05	0.9	balance
C50500	-----	-----	-----	0.05	1.3	balance
C51000	-----	-----	-----	0.05	5.0	balance

Referring to Figure 1, alloys H898 and H899 were cast 10 as ingots with a 15 thickness of 1.75 inch. The ingots were then heated to a temperature of 850°C and held at temperature for 2 hours in air and then hot rolled 12 in six rolling steps to a nominal

thickness of 0.50 inch. The alloys were then cold rolled 14 to a nominal thickness of from 0.090 inch to 0.1 inch and annealed 16 at 575°C for 4 hours. The alloys were then cold rolled to an intermediate gauge 20 as reported in Table 2.

Table 2

Alloy-Process	Intermediate Gauge (inches)	Final Gauge (inches)	Relief Anneal Temperature/Time
H898-A	0.025	0.016	315°/ 2 hours
H898-B	0.032	0.016	315°/ 2 hours
H898-C	0.053	0.016	315°/ 2 hours
H898-D	0.053	0.016	275°/ 2 hours
H899-A	0.025	0.016	315°/ 2 hours
H899-B	0.032	0.016	315°/ 2 hours
H899-C	0.053	0.016	315°/ 2 hours

5

From intermediate thickness 20, the alloys of the invention were annealed 22 at 510°C for three hours and then cold rolled 24 to a  $\Delta$  effective to achieve the final gauge recited in Table 2. A relief anneal, as recited in Table 2, completed alloy processing.

Control alloy C19500 was obtained as a commercial sample in the Hard temper  
 10 and a portion of the control alloy C19500 was relief annealed (RA) at 275°C for 2 hours. The other control alloys C19025, C50500 and C51000 were likewise relief annealed from the Hard temper.

Electrical conductivity values, tensile properties and stress relaxation properties  
 15 were then evaluated and are reported in Table 3. The designation "F" indicates that the properties were measured in the rolled condition, after cold rolling to final gauge 26, but

prior to relief anneal 30. The designation "RA" indicates that the properties were measured following relief anneal 30.

Table 3

Alloy	Electrical Conductivity % IACS	YS* (ksi)	TS* (ksi)	EL* (%)	90° MBR/t (gw/bw)	Percentage Stress Remaining - Long.			
						125° C		150° C	
						1000 hours	3000 hours	1000 hours	3000 hours
H898-A-F	42.6	73	76	3	n.m.	74	72	n.m.	n.m.
H898-A-RA	44.1	66	71	8	0.45/0.45	90	87	80	75
H898-B-F	n.m.	75	78	2	0.7/0.6	n.m.	n.m.	n.m.	n.m.
H898-B-RA	44.6	70	74	8	0.4/0.3	90	86	83	79
H898-C-F	n.m.	82	85	3	0.9/1.1	n.m.	n.m.	n.m.	n.m.
H898-C-RA	43.6	75	80	7	0.4/0.7	n.m.	n.m.	n.m.	n.m.
H898-D-RA	n.m.	78	82	5	n.m.	90	87	80	77
H899-A-F	42.4	74	76	3	n.m.	72	70	n.m.	n.m.
H899-A-RA	43.4	67	72	8	0.45/0.45	87	83	76	70
H899-B-F	n.m.	77	79	3	0.7/0.7	n.m.	n.m.	n.m.	n.m.
H899-B-RA	44.6	70	75	8	n.m.	n.m.	n.m.	n.m.	n.m.
H899-C-F	n.m.	83	86	3	0.9/1.3	n.m.	n.m.	n.m.	n.m.
H899-C-RA	44.1	76	81	7	n.m.	n.m.	n.m.	n.m.	n.m.
C19500 - F	45	81	84	2	0.9/1.1	70	65	59	54
C19500 - RA	45	76	79	5	0.7/0.7	84	79	70	64
C19025 - RA	40	73	76	7	1/1	91	89	82	78
C50500 - RA	48	64	67	4	n.m.	91	85	n.m.	n.m.
C51000 - RA	17	73	85	19	S/1.2	84	79	60	48

5 \* 0.2% offset yield strength/tensile strength/% elongation, 2-inch gauge length

n.m. = not measured

YS = Yield Strength at room temperature

TS = Tensile Strength at room temperature

EL = Elongation at room temperature

10 MBR/t = Minimum Bend Radius/thickness

gw = good way

bw = bad way

15 MBR/t refers to a 90° bend test in which the "good way" bend was made in the plane of the sheet about an axis in the plane of the sheet that is perpendicular to the longitudinal direction (rolling direction) of the sheet during thickness reduction of the strip. The "bad way" bend was made in the plane of the sheet about an axis parallel to the rolling direction. Bend formability was recorded as MBR/t, the minimum bend radius

at which cracking or orange peeling was not apparent, divided by the thickness of the strip.

5 Stress relaxation was evaluated by preloading a strip sample to 80% of the yield strength in a cantilever mode per ASTM (American Society for Testing and Materials) specifications. The strip was heated to either 125°C or 150°C, as specified in Table 3, for the specified number of hours. The higher the stress remaining at the end of the test period, the better the utility of the specified composition for spring applications.

10 The similarity in properties between similarly processed alloys H898 and H899 shows that in the alloys of the invention, a high phosphorus content is not required to achieve the desired properties.

15 Comparing alloy of the invention H898-D-RA with control alloy C19500 in the Relief Anneal temper shows that while the tensile properties are similar (H898-D-RA has a yield strength of 78, a tensile strength of 82 and an elongation of 5% while C19500-RA has a yield strength of 76, a tensile strength of 79 and elongation of 5%), the percentage of stress remaining after 3000 hours exposure to 125°C is significantly higher for alloy 20 898-D-RA (87%) than for C19500 (79%). A more dramatic improvement resistance to stress relaxation is observed after 3000 hours exposure to 150°C. For alloy 898-D-RA, 77% and for C19500-RA, 64%..

25 The alloys of the invention have good thermal stability, that is more of the initially applied stress remains following both 125° and 150°C exposures. Using as an engineering requirement that 70% of the applied stress remain, these alloys are well suited for spring contacts exposed to temperatures up to at least 150°C for at least 3000 hours. This makes the alloys of the invention particularly suitable for under the hood automotive electrical connectors.

25 The stress relaxation behavior of the alloys of the invention is comparable to that of C19025. However, the alloys of the invention have a higher electrical conductivity and better bend formability as noted by the MBR/t values of Table 3. The alloys of the

invention have stress relaxation resistance similar to alloy C50500 with higher strength as noted by the yield strength and tensile strength values of Table 3.

It is apparent that there has been provided in accordance with the invention a copper alloy that fully satisfies the objects, features and advantages set forth hereinabove.

5 While the invention has been described in combination with embodiments thereof, it is evident that many alternatives, modification and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications and variations as fall within the spirit and broad scope of the appended claims.